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Combinative energy, oxygen deficiency and superconductivity in LnBa$_2$Cu$_3$O$_{7-x}$ (Ln=Nd, Er, Sm)*

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The correlation among the combinative energy, superconductivity, oxygen content, the position of holes in different planes, and the position of holes in the Cu(2)-O plane in LnBa$_2$Cu$_3$O$_{7-x}$ (Ln= Nd, Er, and Sm) has been investigated on the basis of a block model. The results indicate that the combinative energy decreases with increasing T_c in all of these compounds. And also, the combinative energies are obviously different with holes at different positions in the Cu(2)-O plane when the oxygen deficiency is low. However, this difference becomes less with increasing the oxygen deficiency. The effect of the holes in different positions on the combinative energy supplies some clue to the understanding of an unresolved problem, i.e. whether the distribution of carriers in the CuO_2 plane is uniform or inhomogeneous. The results not only show that the structural characters, the combinative energy between two structural blocks and the superconductivity are closely interrelated in this class of compounds, but also reveal some differences among these systems. The relationship between the combinative energy and the T_c value in NdBa$_2$Cu$_3$O$_{7-x}$ shows some features different from the systems containing Er or Sm.

Keywords: structure, cohesive energy, superconductivity
PACC: 6150E, 2110D, 7460M

1. Introduction

We have developed a model to deal with the interaction between the two structural blocks, perovskite and rock salt blocks, since most of the high-temperature superconductors have these two blocks. In our previous work,[1] we have successfully established a close relationship among the combinative energy, T_c, and the oxygen content in YBa$_2$Cu$_3$O$_{7-x}$. A highly interesting feature of the superconducting oxide YBa$_2$Cu$_3$O$_{7-x}$ is that it shows a high oxygen nonstoichiometry ($0 \le x \le 1$). In the oxygen-rich side ($x \le 0.2$), it exhibits a superconductivity with a critical temperature of about 90K and has an orthorhombic triple-layered perovskite structure, which is called orthorhombic-I phase. The orthorhombic phase undergoes a transition into a nonsuperconducting tetragonal phase in the oxygen poor side ($x \ge 0.66$).[2] Furthermore, in the intermediate region ($0.3 \le x \le 0.6$), there is another type of orthorhombic phase, called orthorhombic-II phase.[3,4] On the other hand, the compound systems, LnBa$_2$Cu$_3$O$_{7-x}$, constructed by a complete replacement of Y by Ln (lanthanoide elements) in YBa$_2$Cu$_3$O$_{7-x}$, have exhibited similar superconductivity. On the basis of this fact, it is expected that the same correlation mentioned above would also exist in these systems. The aim in this paper is to clarify whether the correlation exists in YBa$_2$Cu$_3$O$_{7-x}$ is specific or it is common in this class of compounds. Here, we take up NdBa$_2$Cu$_3$O$_{7-x}$ ($0 \le x \le 0.9$),[5,7] ErBa$_2$Cu$_3$O$_{7-x}$ ($0 \le x \le 0.74$),[8] and SmBa$_2$Cu$_3$O$_{7-x}$ ($0 \le x \le 0.23$).[9,10] The different regions of the oxygen deficiency are obtained from the experimental data available. The results indicate that the combinative energy and the T_c value in these materials are closely interrelated, similar to

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those in $YBa_2Cu_3O_{7-x}$. But as far as the subtle characters are concerned, $ErBa_2Cu_3O_{7-x}$ is more similar to $YBa_2Cu_3O_{7-x}$ than $NdBa_2Cu_3O_{7-x}$ and $SmBa_2Cu_3O_{7-x}$ are. It is suggested that the differences come from the different properties of rare-earth elements, such as ionic radius, etc., which may affect the arrangement or order of oxygen deficiencies in different ways.

2. Model

The $LnBa_2Cu_3O_{7-x}$ compounds have the CuO_2-Ba- CuO_{2+x}-Ba-CuO_2 plane assembly sandwiched by two layers of the Ln atoms. We take $LnBa_2Cu_3O_{7-x}$ "molecule" (i.e., formula unit) as a cell. It is treated as two blocks, the so-called perovskite and rock salt blocks. The perovskite block is the active block where

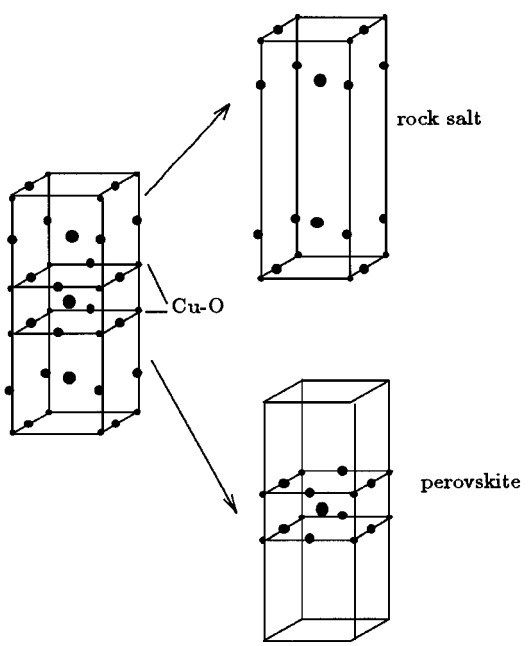


Fig.1. The division of the two blocks in $LnBa_2Cu_3O_{7-x}$ (Ln=Nd, Er, Sm).

the Cu(2)-O planes are located and the carriers concentrate. The rock salt block is the so-called reservoir block, which provides the Cu(2)-O planes with carriers. The division of the two blocks is shown in Fig. 1. The interaction between the two blocks is measured by combinative energy which is defined as: the combinative energy between the two blocks = the cohesive energy of the whole cell − the cohesive energy of the perovskite block − the cohesive energy of the rock salt block. The detail of the calculation method has been described in Ref. [11].

3. Correlation among oxygen content, T_c value, and combinative energy

We follow the notation in Refs. [5–7] for various ion positions in the structure of $NdBa_2Cu_3O_{7-x}$ and use the values of the lattice parameters in them. Similarly, the experimental data for $ErBa_2Cu_3O_{7-x}$ are taken from Ref. [8] and for $SmBa_2Cu_3O_{7-x}$ from Refs. [9,10]. The structural parameters of $SmBa_2Cu_3O_{7-x}$ with high oxygen deficiency are not available. The calculated results in this paper show that $SmBa_2Cu_3O_{7-x}$ has the similar trend as the other systems in low oxygen deficiency region, which may be useful for understanding some properties of this class of compounds in this oxygen content region.

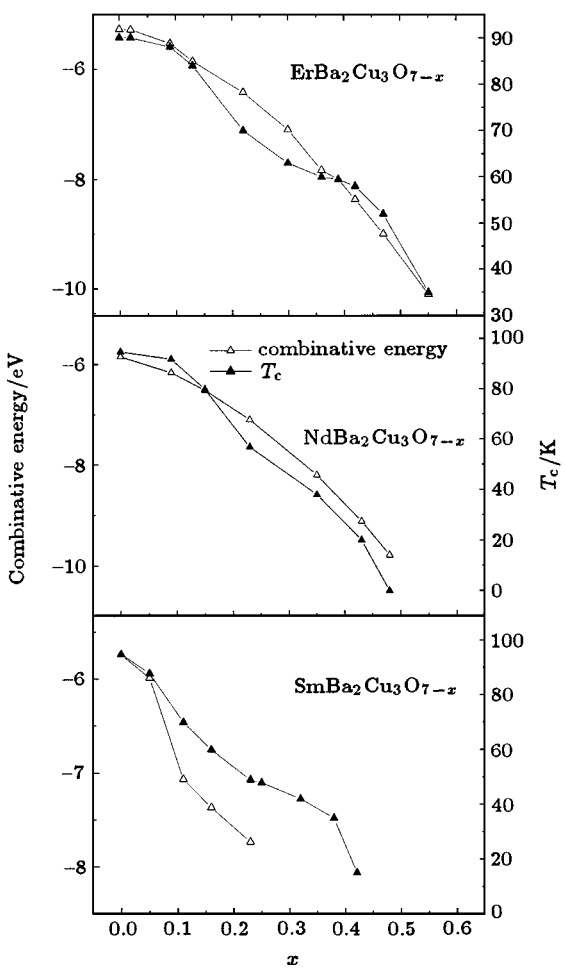


Fig.2. The combinative energy and the value of T_c (triangles) versus x in $LnBa_2Cu_3O_{7-x}$ (Ln= Nd, Er, Sm) with holes at the position where the Cu ion locates in the Cu(2)-O plane, namely at position (0, 0) as shown later.

As shown in Fig. 2, we find that in all the systems, the combinative energy decreases with increas-

ing T_c and increasing the oxygen deficiency. This is consistent with the behaviour in the Y- system.[1] To show this relation more clearly, the curves of combinative energy versus T_c are plotted in Fig. 3.

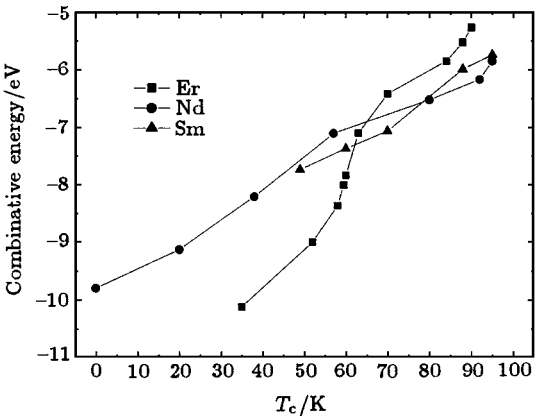


Fig.3. The curves of T_c versus combinative energy in LnBa$_2$Cu$_3$O$_{7-x}$ (Ln= Nd, Er, Sm).

It is well known that T_c is affected dramatically by subtle changes in oxygen content in the Ln Ba_2 Cu_3 O_{7-x} systems. The T_c value decreases with increasing x in all the systems. Here, we will show that the oxygen content also plays an important role in the interaction between the two blocks in Ln Ba_2 Cu_3O_{7-x}. Accordingly, it is speculated that combinative energy is somewhat intimately related to the high-temperature superconductivity. It is noted that there are plateaux in the curves of T_c versus x (in Ref. [8]) and those of combinative energy versus x in $ErBa_2$ Cu_3O_{7-x}[2] (as shown in Fig. 2) and YBa_2 Cu_3 O_{7-x}.[1] In contrast, there are no such kinds of characteristics in $NdBa_2$ Cu_3 O_{7-x}. This difference might result from the difference of ionic size, which will be discussed in detail later.

4. Effects of the distribution of holes in different planes

One of the most striking features of the high-temperature superconductor is that these materials are quasi-two dimensional. The key structural unit is the CuO_2 plane, which extends in the a–b directions, and the interplane coupling is very weak. To show whether our model could reflect this property of these materials, we calculated the combinative energy between the two blocks in these systems with the holes in the Cu (2)-O plane, in the Cu(1)-O plane (where the Cu-O chain locates) and in the Ba-O plane. It can be seen from Fig. 4 that, in contrast to the case when the holes are in the Ba-O plane, there is a close connection between the combinative energy and the T_c value in all the materials when the holes are in the Cu(2)-O plane. A similar relationship also exists when the holes are in the Cu(1)-O plane. The distinction of the combinative energy when holes at different planes is less obvious in high oxygen deficiency region than that in low oxygen deficiency region. When oxygen deficiency content is low, the energy difference between the Ba-O plane and the Cu(2)-O plane is large (about 15–20eV), which could be a barrier to the interplane movement of the carriers between the Ba-O plane and the Cu(2)-O plane. This is in agreement with the experimental facts that the carriers are mainly in the Cu(2)-O plane. The energy difference between the Cu(1)-O plane and the Cu(2)-O plane is not so large.

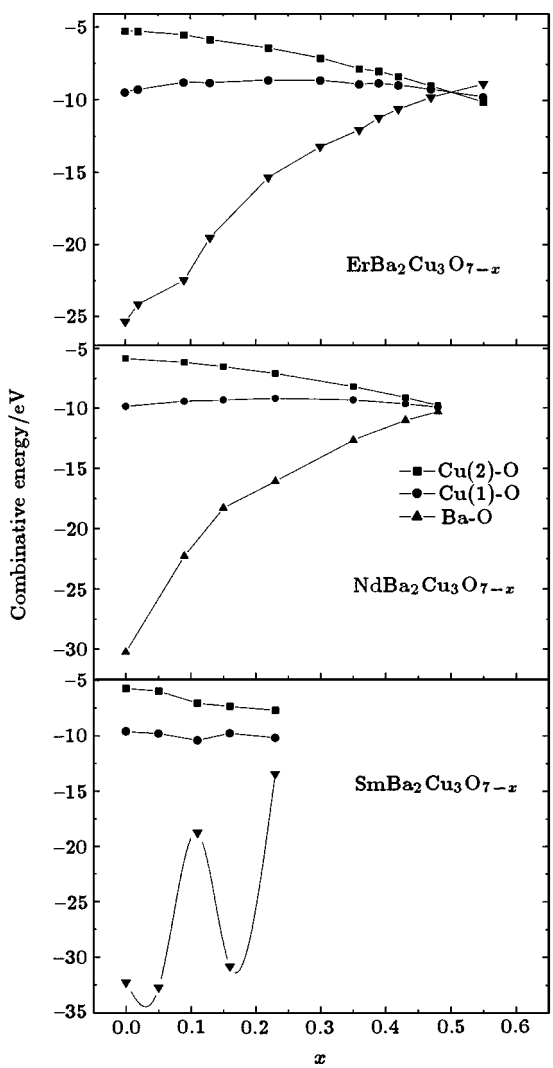


Fig.4. The curves of combinative energy versus x with holes at different planes.

5. Effects of the distribution of holes in the Cu(2)-O plane

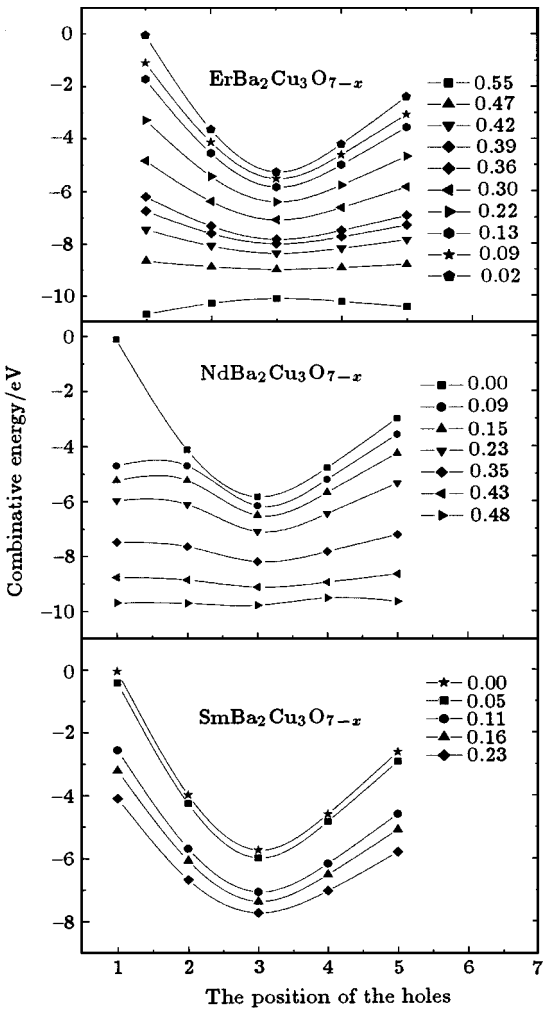


Fig.5. The combinative energy versus the position of the holes in LnBa$_2$Cu$_3$O$_{7-x}$ (Ln= Nd, Er, Sm) with different oxygen deficiency. The insets show the oxygen deficiency content and the positions of the holes in the Cu(2)-O planes. The coordinates of them are as follows: 1 (0.5,0.5), 2 (0.5,0), 3 (0,0), 4 (0.25,0) and 5 (0.25,0.25).

With the improved experimental techniques, the important role of inhomogeneity, such as incommensurate fluctuations[12,13] and incommensurate magnetic fluctuations[14], etc., has been recognized. In order to find out the effects of the position of holes in the Cu(2)-O plane on the combinative energy between the two blocks, the combinative energy in LnBa$_2$Cu$_3$O$_{7-x}$ (Ln=Nd, Er, Sm) with different x versus the position of the holes are plotted in Fig. 5. It is obvious that the energy is different when the holes are concentrated at different positions in the Cu(2)-O plane. An unresolved problem is whether the distribution of carriers in the Cu(2)-O plane is uniform or inhomogeneous. The energy difference with holes at different positions may hint something to this problem. Since the stripe fluctuation is related to the movement of the carriers from one position to another, if there were no energy difference among the positions, the transition of carriers from one place to the other should be equal, and the stripe fluctuation should be regular. Nevertheless, our results show that the different positions are not equivalent as far as the energy is concerned. According to this, we suggest that the incommensurate stripe fluctuation has something to do with the energy difference in different positions in the Cu(2)-O plane.

Moreover, there are two very conspicuous features in Figs. 4 and 5. That is, the energies of all the positions seem to be identical for x=0.48 in NdBa$_2$ Cu$_3$ O$_{7-x}$ and x=0.47 in ErBa$_2$ Cu$_3$O$_{7-x}$, even if the holes are in different planes (as shown in Fig. 4).

The value of the combinative energy in this case remains the same no matter where the holes locate. Similar situation can be found in YBa$_2$Cu$_3$O$_{7-x}$ for x=0.59.[1] Are these features related to the vanishing of the superconductivity in these systems? The superconductivity disappears at x=0.45 in NdBa$_2$Cu$_3$ O$_{7-x}$,[7] at x=0.7–0.75 in ErBa$_2$Cu$_3$O$_{7-x}$,[8] and at x=0.66 in YBa$_2$Cu$_3$O$_{7-x}$.[14] We therefore suggest that the crossing of the different curves in Fig. 4 might have something to do with the disappearance of the superconductivity, but the former might not be responsible for all of the latter. Therefore, further study is badly needed for this phenomenon.

It is noticed that the behaviour of NdBa$_2$Cu$_3$ O$_{7-x}$ is somewhat different from the other two systems. The oxygen deficiency is almost the same at which the value of the combinative energy for different planes becomes the same (x=0.48) and the superconductivity disappears (x=0.45). The corresponding values of x in ErBa$_2$Cu$_3$O$_{7-x}$ are 0.47 and 0.7–0.75; and they are 0.59 and 0.66 in YBa$_2$Cu$_3$O$_{7-x}$. The system of NdBa$_2$Cu$_3$O$_{7-x}$ always shows some difference from the other two systems although they have the similar crystalline structure. We try to understand the difference from the radii of lanthanide. The eightfold coordinated trivalent Y, Er, Nd, and Sm have radii of 1.02, 1.00, 1.09 and 1.12′ and the sixfold coordinated trivalent of them have radii of 0.89, 0.88, 0.96 and 1.00′, respectively. Interestingly, it is noticed that the radii of the eightfold coordinated Y^{3+} and Er^{3+} can match the ionic radii of the sixfold coordinated Nd^{3+} and Sm^{3+}. Assume that in NdBa$_2$Cu$_3$O$_{7-x}$

system Nd^{3+} tends to be sixfold coordinated, which may result in decreasing oxygen in the Cu(2)-O plane. It is well known that in the Y-system the change of oxygen takes place in the Cu(1)-O plane. This may be the reason for the different behaviours between $YBa_2Cu_3O_{7-x}$ and $NdBa_2Cu_3O_{7-x}$.

Although there are differences among these materials mentioned above, we can see the same tendency that T_c decreases with increasing the interaction between the two blocks in all the systems. This indicates that the strength of the attraction between the two blocks contributes to the depression of the superconductivity in these systems. The combinative energy reflects the strength between the two blocks. So the lower the combinative energy, the looser the combination between the two blocks and the higher the T_c value.

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